Heterogeneous decay of metastable phase on various centers -2

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Abstract

A system of a metastable phase with several sorts of heterogeneous centers is considered. An analytical theory for the process of decay in such a system has been constructed. The free energy of formation of a critical embryo is assumed to be known in the macroscopic approach. At first all asymptotic cases are investigated and then a general intermediate solution is suggested. All approximate transformations are accomplished with the corresponding numerical estimates and analytical justifications. This is the second part of the manuscript, the first part can be also found in this archive.

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1 Intermediate approximate solution for several sorts of centers

In the case of nucleation on one sort of centers the expression for $g_i(z)$ is unknown only when the spectrum is cut off by exhaustion of heterogeneous centers. So, one doesn't know it in the situation when the converging force of the operator S_i is very strong. In the case of the several sorts of centers the situation is another. One doesn't know every term in $\sum_j g_j(z)$. Then one can come to the situation where according to the first iteration the spectrum is cut off by the exhaustion of supersaturation initiated by droplets formed on some sort of centers but in reality all heterogeneous centers of that sort are exhausted and those droplets practically don't consume the vapor (due to their quantity). So, it is necessary to have some more precise expression for g_i which allows to calculate the next iteration for θ_i.

1.1 Mono-disperse approximation

The length corresponding to the cut-off of the spectrum by the substance exhaustion is practically one and the same for all sorts of the droplets (all Γ_i have approximately one and the same value[1]). Analyzing the subintergal expression in the equation for g_i in the pseudo homogeneous case one can see that the subintegral expression $s = (z-x)^3 \exp(-\Gamma_i \sum_j g_j/\Phi_*)$ connected with a variation of the supersaturation in the formula for g_i is a very sharp function of x. It is less than the function

$$s_{bel} = \Theta(z-x)(z-x)^3 \tag{1}$$

and greater than the function

$$s_{ab} = \Theta(z-x)(z-x)^3 \exp(-\frac{\Gamma_i \sum_j f_{*j}}{\Phi_*}\frac{x^4}{4}) \quad . \tag{2}$$

Fig. 6 illustrates the behavior of the values s_{ab} and s_{bel}. It can be seen that they practically coincide. This is the reason of applicability of the first iteration as a good approximation for the precise solution for one sort of centers.

Let us introduce an approximation for this function. One has to extract the region of the sizes of the droplets which are essential in the vapor consumption. This consumption is essential when

$$z \approx \Delta x \tag{3}$$

where Δx is the length of the cut-off by the supersaturation. Certainly, the sizes of the droplets which are essential in the vapor consumption must be smaller than Δx because the effectiveness of the iteration procedure in the homogeneous case is based on the fact that the droplets formed at the almost ideal supersaturation determine the formation of the spectrum. One can see that s is a very sharp function of x and this is the reason for the monodisperce approximaion for s. Now one has to define characteristics of this approximation.

[1] Alternative situations correspond to the asymptotic cases and have been already described.

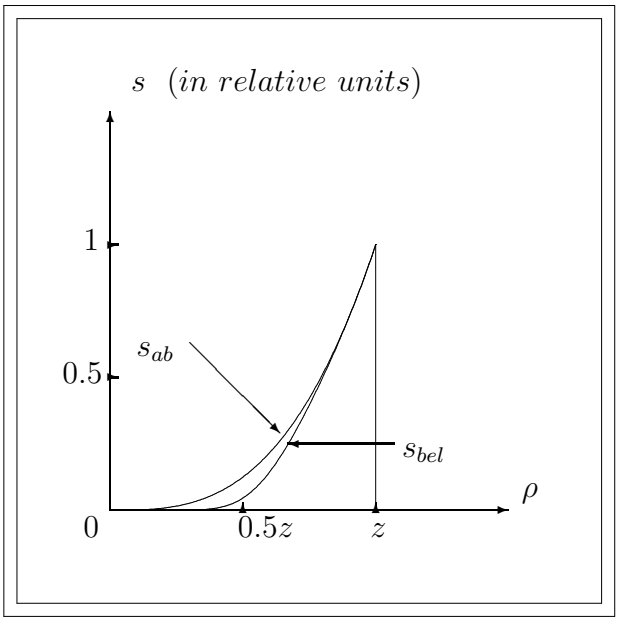

Figure 6.
Functions s_{ab} and s_{bel}.

The condition for the differential width is that the subintegral function falls two times in comparison with an amplitude value. For the differential half-width $\delta_{1/2}x$ one can get the following expression

$$\delta_{1/2}x = (1 - \frac{1}{2^{1/3}})x \quad . \tag{4}$$

The integral half-width $\Delta_{1/2}x$ can be obtained from the corresponding equation

$$N_{ess}x^3 = f_{*\,i}\frac{x^4}{4}n_\infty \quad , \tag{5}$$

where N_{ess} is the characteristic number of the droplets obtained as $N_{ess} = f_{*\,i}\Delta_{1/2}xn_\infty$ and the r.h.s. of the previous equation is the first iteration approximation. This gives

$$\Delta_{1/2}x = \frac{1}{4}x \tag{6}$$

and it practically coincides with $\delta_{1/2}x$.

The subintegral function s is now decomposed into the essential part where

$$x \leq \frac{z}{4}$$

and the tail where

$$x \geq \frac{z}{4}$$

The tail will be neglected and due to the small relative size of the essential part the mono-disperse approximation of sizes for the droplets in the essential part will be used. As the result one can get an approximation

$$g(z) = \frac{N(z/4)}{n_\infty} z^3 \quad , \tag{7}$$

where $N(z/4)$ is the number of the droplets appeared from $x = 0$ till $x = z/4$.

Since the spectrum is cut off by the exhaustion of the supersaturation in a frontal (sharp) manner, the value of g_i is unessential before $z = \Delta x$ because it is small. After the moment of the cut-off it is unessential also because there is no formation of the droplets. So, instead of the previous approximation one can use

$$g_i(z) = \frac{N_i(\Delta_i x/4)}{n_\infty} z^3 \quad . \tag{8}$$

Now let us turn to the heterogeneous case. The exhaustion of heterogeneous centers makes the subintegral function more sharp and the mono-disperse approximation becomes at $x \sim \Delta_i x$ even better than in the pseudo homogeneous situation. Certainly, one has to use $N(\Delta_i x/4)$ calculated with account of exhaustion of heterogeneous centers (but at the coordinate, obtained without any account of exhaustion of heterogeneous centers).

Fig. 7 illustrates the form of the spectrum on the base of "mono-disperse approximation". The case of the pseudo homogeneous condensation is considered. Three curves are drawn: the spectrum in the mono-disperse approximation f_{appr} ; the spectrum in the first iteration f_1 which can be considered as a very precise approximation and the numerical solution f. Two of them f and f_1 coincide and correspond to a thick line. The back side in the first iteration is more sharp than in the "mono-disperse approximation". Nevertheless the deviation isn't so essential. It can be eliminated by a perturbation theory.

One can get $N(\Delta_i x/4)$ from the solution of the equations for the separate condensation process because only the lowest length of the cut-off is nesessary. This length is given without any cross influence taking into account due to the frontal character of the back side of the spectrum. Then one has to repeat this procedure with the already known N_i.

1.2 Final iterations

Now one can see a way to solve the system of the condensation equations.

A. Method of separate lengths.

At first one has to solve equations for all separate nucleation processes

$$g_i = f_{*\,i} \int_0^z (z-x)^3 \exp(-\Gamma_i \frac{g_i}{\Phi_*}) \theta_i dx \equiv G_i(g_i, \theta_i) \quad , \tag{9}$$

$$\theta_i = \exp(-f_{*\,i} \frac{n_\infty}{\eta_{tot\ i}} \int_0^z \exp(-\Gamma_i \frac{g_i}{\Phi_*}) dx) \equiv S_i(g_i) \tag{10}$$

for every i. This solution is given by the standard iteration procedure. In the second approximation one can calculate the value of $\theta_{(2)}(\Delta_i x/4)$ explicitly

$$\theta_{i(2)}(\Delta_i x/4) = \exp(-f_{*\,i} \frac{n_\infty}{\eta_{tot\ i}} \int_0^{\Delta_i x/4} \exp(-\frac{\Gamma_i f_{*\,i}}{4\Phi_*} z^4) dx) = \exp(-f_{*\,i} \frac{n_\infty}{\eta_{tot\ i}} (\frac{\Gamma_i f_{*\,i}}{4\Phi_*})^{-1/4} C) \ , \tag{11}$$

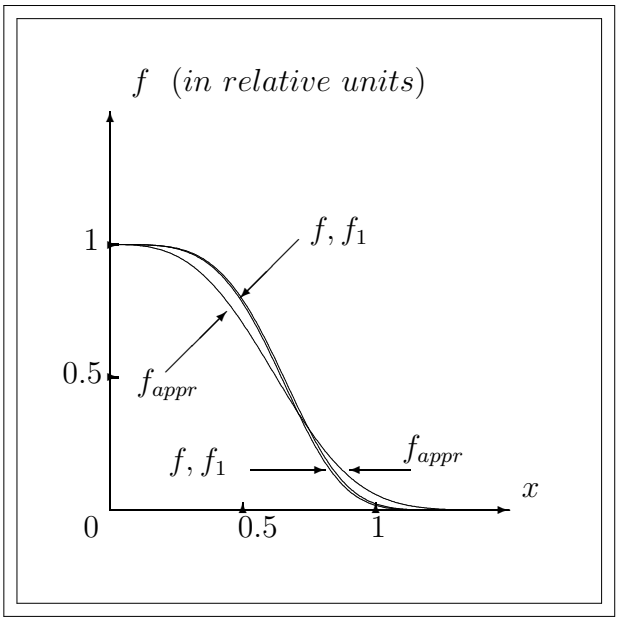

Figure 7.
Functions f, f_1 and f_{appr}.

where

$$C = \int_0^{1/4} \exp(-z^4)dx \approx 0.25 \quad . \tag{12}$$

Then

$$N_{i(2)}(\Delta_i x/4) = \eta_{tot\ i}(1 - \theta_{i(2)}(\Delta_i x/4)) \quad . \tag{13}$$

One has to fulfil these calculations for every sort of the heterogeneous centers. Considering these approximations as the initial ones it is necessary to do only one more step of the iteration procedure to get the suitable results. They will be marked as the 'final' ones. One has to calculate $\theta_{i\ final}(\infty)$ and $N_{final\ i}(\infty)$

$$\theta_{i\ final}(z) = \exp[-f_{*\ i}\frac{n_\infty}{\eta_{tot\ i}}\int_0^z \exp(-\frac{\sum_j \Gamma_i N_{j\ (2)}(\Delta_j x/4)}{n_\infty \Phi_*}x^3)dx] \quad , \tag{14}$$

$$N_{final\ i}(\infty) = \eta_{tot\ i}[1 - \exp(-f_{*\ i}\frac{n_\infty}{\eta_{tot\ i}}(\frac{\sum_j \Gamma_i N_{j\ (2)}(\Delta_j x/4)}{n_\infty \Phi_*})^{-1/3}B] \quad . \tag{15}$$

These expressions are valid under the reasonable separation of heterogeneous centers into sorts when the centers with approximately one and the same height of the activation barrier are considered as one sort. Meanwhile it is obvious that when one splits one sort into very many sub-sorts then one can formally attain a wrong result.

Let us suppose that the number of heterogeneous centers ensures $h_i \gg 1$, i.e. the fall of the supersaturation leads to the interruption of formation of the droplets. One can split this sort into so many sub-sorts (j) that for every sub-sort $h_{ij} \ll 1$, i.e. one can see the exhaustion of

the sub-sort in the separate process of the condensation. Moreover, one can assume that this exhaustion is finished before z attains the quarter of the length of the spectrum initiated by the fall of the supersaturation. Since $\Delta_{ij}x$ is proportional to $\eta_{ij\ tot}^{-1/4}$ (where $\eta_{ij\ tot}$ is the total number of the centers of the given sub-sort) and $\delta_{ij}x$ doesn't depend on this quantity, the required property is obvious. Then after the summation over all sub-sorts one can see that the total number of the droplets formed up to $\Delta_i x/4$ coincides with the total number of the heterogeneous centers. This conclusion is wrong.

The reason of the error is that the width of the spectrum is smaller than the width in the process of the separate formation. Evidently, the mono-disperse approximation doesn't work at such distances. Under the reasonable definition of the heterogeneous sorts all characteristic lengths are different. So, ordinary, there is no such effect in this situation. But still one has to correct these results. The simplest way is to consider all centers with the difference in the activation barrier height less than one thermal unit as one and the same sort. This solves the problem, but this requirement is rather artificial.

Now these results will be corrected in more elegant way. The mono-disperse approximation leads to some already defined functional form for g and for ζ. The form is already known and now only parameters in these functional dependencies have to be determined.

B. Method of the unique length.

The unique length of the spectrum Δx will be chosen. At this very moment Δx is unknown, but satisfies the following inequality:

$$\Delta x \leq \Delta_i x$$

for every sort of the heterogeneous centers. This leads to

$$g_i(z) = \frac{N_i(\Delta x/4)}{n_\infty} z^3 \quad , \tag{16}$$

which gives

$$N_{i(2)}(\Delta x/4) = \eta_{i\ tot}(1 - \theta_{i(2)}(\Delta x/4)) \quad , \tag{17}$$

$$\theta_{i\ (2)}(\Delta x/4) = \exp[-f_{*\ i}\frac{n_\infty}{\eta_{tot\ i}}\int_0^z \exp(-\frac{\Gamma x^3}{\Phi_* n_\infty}\sum_j N_j(\Delta x/4))dx] \quad . \tag{18}$$

The weak dependence $\Gamma_i \approx \Gamma$ on the sort of the centers is neglected here for simplicity, while the strong dependence f_{*i} on the sort of centers is taken into account. After the substitution one can get the system of the algebraic equations for $N_i(\Delta x/4)$

$$N_i(\Delta x/4) = \eta_{i\ tot}(1 - \exp(-f_{*\ i}\frac{n_\infty}{\eta_{tot\ i}}\int_0^{\Delta x/4} \exp(-\frac{\Gamma}{\Phi_*}\frac{x^3}{n_\infty}\sum_j N_j(\Delta x/4))dx)) \quad . \tag{19}$$

Let us simplify the last system. To calculate the integral one can note that

$$\int_0^x \exp(-x^3)dx \approx x \qquad x \leq 1/4 \quad . \tag{20}$$

So, the trivial dependence of the r.h.s. on N_j disappears. One can come to

$$N_i(\Delta x/4) = \eta_{i\ tot}(1 - \exp(-f_{*\ i}\frac{n_\infty}{\eta_{tot\ i}}\frac{\Delta x}{4})) \quad . \tag{21}$$

On the other hand one can use the sense of Δx as the half-width of the spectrum due to the fall of the supersaturation:

$$\frac{\Delta x^3}{n_\infty}\sum_j N_i(\Delta x/4)\frac{\Gamma}{\Phi_*}=1 \quad . \tag{22}$$

After the substitution one can get the equation for Δx

$$\frac{\Delta x^3}{n_\infty}\sum_j \eta_{j\ tot}(1-\exp(-f_{*\ j}\frac{n_\infty}{\eta_{tot\ j}}\frac{\Delta x}{4}))\frac{\Gamma}{\Phi_*}=1 \quad . \tag{23}$$

To solve this algebraic equation one can choose the initial approximation as a solution of the following equation

$$\frac{\Delta x^4}{4}\sum_j f_{*\ j}\frac{\Gamma}{\Phi_*}=1 \quad . \tag{24}$$

Iterations are constructed according to

$$\frac{\Delta_{(i)}x^3}{n_\infty}\sum_j \eta_{j\ tot}(1-\exp(-f_{*\ j}\frac{n_\infty}{\eta_{tot\ j}}\frac{\Delta_{(i-1)}x}{4}))\frac{\Gamma}{\Phi_*}=1 \quad . \tag{25}$$

When the last equation is solved then equation (21) expresses $N_i(\Delta x/4)$ through Δx and solves the problem. Equation (16) gives the expression for g_i and for the supersaturation as the function of time.

One can estimate the relative error by the pseudo homogeneous case which leads to

$$\frac{\mid N_i(\infty)-N_{final\ i}(\infty)\mid}{N_i(\infty)}\le\frac{\mid A-B\mid}{A}\sim 0.02 \tag{26}$$

The investigation of the process of nucleation on several sorts of heterogeneous centers is completed.

2 Solution for heterogeneous centers with quasi continuous activity

2.1 Iteration procedure

The smoothness of $\eta(w)$ is supposed here. It allows to hope that the cross influence of exhaustion of one type of heterogeneous centers on the cut-off of the droplets formation on another sort of centers will be not so strong and one can apply some modifications of the standard iteration procedure. It can be constructed in a following way: for initial approximations one can choose

$$g_0(z,w)=0 \quad , \qquad \theta_0=1 \quad ; \tag{27}$$

the recurrent procedure is defined according to

$$g_{i+1}(z,w)=G_w(g_i^{tot},\theta_i(w)) \quad , \qquad g_i^{tot}(z)=\int dw g_i(z,w) \quad . \tag{28}$$

$$\theta_{i+1}(z,w) = S_w(g_i^{tot}) \tag{29}$$

The monotonic properties of G_w, $\int dw$ and S_w lead to the chains of inequalities analogous to (**??**)-(**??**), which ensure estimates for precision of approximations. Certainly, to calculate iterations one has to use some expression for $\eta_{tot}(w)$. So, at first one has to consider the limit cases and obtain some estimates.

One can see the absence of η_{tot} in the r.h.s. of (29). So, for arbitrary η_{tot} the power of exhaustion will be determined only by w. The centers with the high activity w are almost exhausted during the process of the condensation. The centers with the relatively small activity w remain free. The intermediate region has rather small size. To give the qualitative estimates one can see that the supersaturation ζ appears only in the function f_ζ. For f_ζ one can obtain the following estimate

$$f_\zeta \sim f_* \exp(-const x^\epsilon) \qquad 3 \le \epsilon \le 4 \tag{30}$$

This estimate goes from the obvious fact that the spectrum of the droplets must be wider than the mono-disperse one and the intensity of nucleation must decrease in time. On the base of the last estimates one can see that the width Δx of the spectrum is a well defined value.

The rough approximation for exhaustion of heterogeneous centers can be obtained from the first approximation in the iteration procedure

$$\theta = \exp[-f_* \exp(\lambda w) n_\infty z] \tag{31}$$

and for the value at the end of nucleation period

$$\theta_{final} = \exp[-f_* \exp(\lambda w) n_\infty \Delta x] \quad . \tag{32}$$

One can define $w_<$ and $w_>$ according to

$$w_< = w_0 - \frac{\epsilon}{\lambda} \quad , \qquad w_> = w_0 + \frac{\epsilon}{\lambda} \quad , \tag{33}$$

where

$$w_0 = \frac{1}{\lambda} \ln(\frac{\ln 2}{f_* n_\infty \Delta x}) \quad , \quad \epsilon \sim 1 \quad . \tag{34}$$

These constructions are illustrated in Fig. 8. For $w > w_>$ almost all heterogeneous centers are exhausted. For $w < w_<$ almost all heterogeneous centers remain free. This remark allows to rewrite the expression for g^{tot} in the following form

$$g^{tot} = \int_{w_<}^{w_>} dw g(z,w) + \int_{w_>}^{\infty} \eta_{tot}(w) dw \frac{z^3}{n_\infty} \quad . \tag{35}$$

The size of the intermediate region corresponds to a variation of w of an order $1/\lambda$ or to the variation of ΔF in one thermal unit. Since $\Delta F \gg 1$, the relative variation of ΔF in the intermediate region is small. So, it is reasonable to put in this region

$$\eta_{tot}(w) = \eta_* = const \quad . \tag{36}$$

One can spread this approximation over the region $w > w_>$ because the behavior of η_{tot} for these centers isn't important. Only $\int \eta_{tot} dw$ over this region is essential. Certainly, one has to get the boundary w_{max} of this region by

$$\int_{w_>}^{w_{max}} \eta_* dw = \eta_*(w_{max} - w_>) = \int_{w_>}^{\infty} \eta_{tot}(w) dw \quad . \tag{37}$$

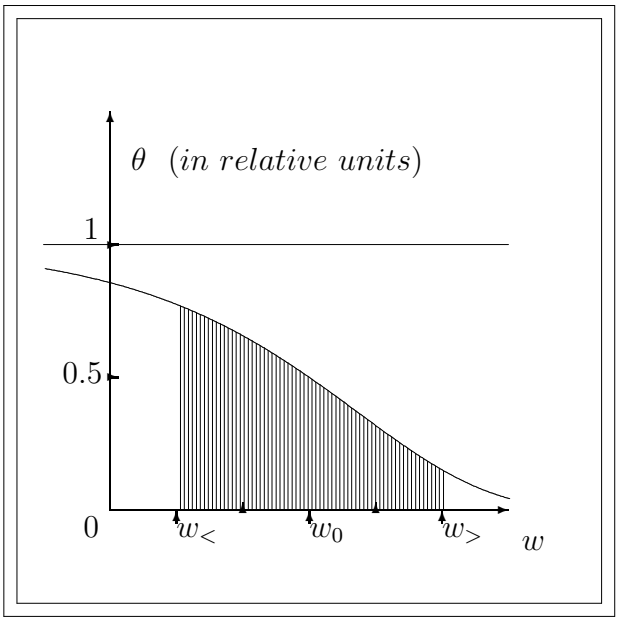

Figure 8.
Function θ and boundaries $w_<$, $w_>$.

For $w < w_<$ the accuracy of this approximation is not so essential because these centers remain free.

After the scale transformations $\Gamma g^{tot}/\Phi_* \to G$; $\Gamma g/\Phi_* \to g$

$$g = \frac{\Gamma f_* \eta_*}{\Phi_*} \exp(\lambda w) \int_0^z (z-x)^3 \exp(-G)\theta dx \quad , \tag{38}$$

$$G = \int_{-\infty}^{w_{max}} dw g \quad , \tag{39}$$

$$\theta = \exp[-f_* n_\infty \exp(\lambda w) \int_0^z \exp(-G) dx] \quad . \tag{40}$$

By the appropriate shift of w one can put w_{max} to the zero. In the appropriate scale of w one can put $\lambda = 1$. In the appropriate scale of z one puts the coefficient in (38) to unity. As the result, only one parameter - the coefficient $f_*^{3/4} \exp(3\lambda w_{max}/4) \Phi_*^{1/4}/(\Gamma^{1/4} \eta_*^{1/4})$ remains in the last equation. One can mark it by A and get

$$g = \exp(w) \int_0^z (z-x)^3 \exp(-G)\theta dx \quad , \tag{41}$$

$$G = \int_{-\infty}^{0} dw g \quad , \tag{42}$$

$$\theta = \exp[-A \exp(w) \int_0^z \exp(-G) dx] \quad . \tag{43}$$

An iteration procedure can be constructed as

$$g_{i+1} = \exp(w) \int_0^z (z-x)^3 \exp(-G_i)\theta_i dx \quad , \tag{44}$$

$$G_i = \int_{-\infty}^0 dw g_i \quad , \tag{45}$$

$$\theta_{i+1} = \exp(-A \exp(w) \int_0^z \exp(-G_i) dx) \quad , \tag{46}$$

$$g_0 = 0 \quad , \quad \theta_0 = 1 \quad . \tag{47}$$

In the first iteration

$$g_1 = \exp(w) \frac{z^4}{4} \quad , \tag{48}$$

$$G_1 = \int_{-\infty}^0 dw g_1 = \frac{z^4}{4} \quad , \tag{49}$$

$$\theta_1 = \exp(-A \exp(w) z) \quad . \tag{50}$$

The second approximation gives for θ the following result

$$\theta_2 = \exp[-A \exp(w) \int_0^z \exp(-\frac{z^4}{4}) dz] \quad , \tag{51}$$

then for the final value

$$\theta_{final\ 2} = \exp[-A \exp(w) 1.28^{1/4}] \tag{52}$$

and for N^{tot}

$$N^{tot} = \int_{-\infty}^0 [1 - \exp(-Aexp(w) 1.28^{1/4})] dw \eta_* \quad . \tag{53}$$

For g in the second approximation

$$g_2 = \exp(w) \int_0^z (z-x)^3 \exp(-A \exp(w) x) \exp(-x^4/4) dx \quad . \tag{54}$$

The analytical expression for g_2 and further iterations can not be calculated.

2.2 Universal solution

The system of equations (41) - (43) doesn't allow the universal solution as in the case of homogeneous condensation when (41) hasn't θ in the r.s.h.. But the operator in the r.h.s. of (41) ensures a rapid convergence of the iterations. The worst situation for the iteration convergence is $A = 0$. In this situation one has after rescaling the universal system

$$g = \exp(w) \int_0^z (z-x)^3 \exp(-G) dx \quad , \tag{55}$$

$$G = \int_{-\infty}^0 g dw \quad . \tag{56}$$

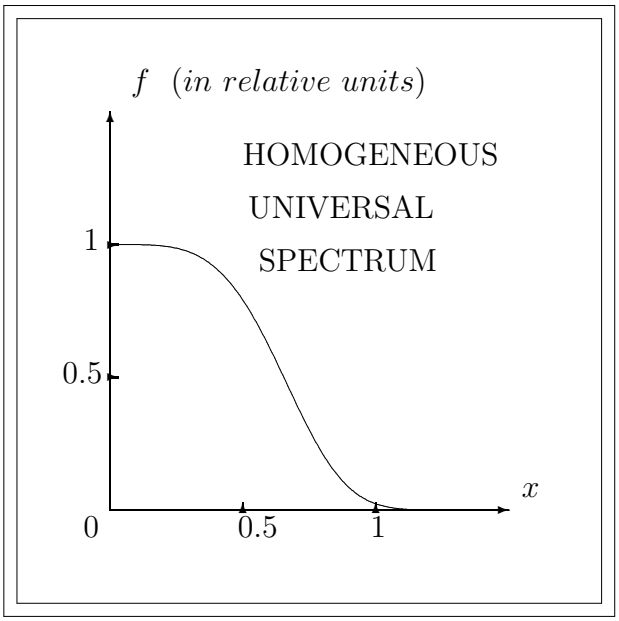

Figure 9.
Universal form of spectrum in the pseudo homogeneous case.

This system has the universal solution[2] which will be marked by G_0. This universal form of the size spectrum is shown in Fig. 9.

The evolution is determined by the first three momentums (and the zero one) of the distribution function

$$\mu_i(z) = \int_0^z x^i \exp(-G)\theta dx \quad , \qquad i = 0, 1, 2, 3 \tag{57}$$

and in the pseudo homogeneous case it is determined by

$$\mu_i(z) = \int_0^z x^i \exp(-G_0) dx \quad . \tag{58}$$

After the end of the short period of intensive formation of droplets one can substitute in (57) and (58) ∞ instead of z in the region of the integration. So, the further evolution will be determined by four constants[3] $\mu_i(\infty)$ $i = 0, 1, 2, 3$. If one takes for G the universal solution G_0 (when $A = 0$) then the values of μ_i are the universal constants which can be obtained by the unique numerical solution of the last system.

Now one has to return to the iteration procedure. One can use G_0 as the initial approximation in the iteration procedure and get

$$\theta_1 = \exp[-A \exp(w) \int_0^z \exp(-G_0) dx] \quad , \tag{59}$$

$$g_2 = \exp(w) \int_0^z (z - x)^3 \exp(-G_0) \exp(-A \exp(w) \int_0^x \exp(-G_0) dx') dx \quad , \tag{60}$$

[2]The trivial integration over w leads to the equation analogous to the homogeneous case.
[3]The main influence is due to μ_0.

$$G_2 = \int_{-\infty}^{0} \exp(w) \int_0^z (z-x)^3 \exp(-G_0) \exp(-A \exp(w) \int_0^x \exp(-G_0) dx') dx dw \quad . \tag{61}$$

The decomposition of exponents gives

$$G_2 = \sum_{i=0}^{\infty} \frac{(-A)^i}{(i+1)!} P_i(z) \quad , \tag{62}$$

where

$$P_i = \int_0^z (z-x)^3 \exp(-G_0) J_{00}^i(x) dx \quad , \tag{63}$$

$$J_{00}(x) = \int_0^x \exp(-G_0) dx \quad . \tag{64}$$

Then the function $B(z) = \int_0^z \exp(-G_2(x))dx$ at $z = \infty$ will be the following

$$B(z=\infty) = A \int_0^{\infty} \exp(-G_2) dx = A \int_0^{\infty} \exp(-P_0(z)) \exp(-\sum_{i=1}^{\infty} \frac{(-A)^i}{(i+1)!} P_i(z)) dz \quad . \tag{65}$$

The decomposition of the last exponent leads to

$$B(z=\infty) = \prod_{i=1}^{\infty} \sum_{j=0}^{\infty} \frac{(-1)^j}{j!} A \frac{(-A)^{ij}}{((i+1)!)^j} C_{ij} \quad , \tag{66}$$

where

$$C_{ij} = \int_0^{\infty} \exp(-P_0(x)) P_i^j dx \tag{67}$$

are the universal constants. For the total number of the droplets with a given activity

$$N_{tot}(w) = \eta_* (1 - \exp(-B(z=\infty) \exp(w))) \quad . \tag{68}$$

In the same manner one can take into account the deviation of η_* from a constant value. After the decomposition of η_* into Tailor series one can take the initial approximation as G_0 and act in the manner similar to (59) - (68). As a result, some expansions in the powers of the parameter A, the derivatives of η_{tot} and the universal constants can be seen.

Fig. 10 illustrates these constructions. Here the most interesting function $I_{00} = \int_0^{\infty} \exp(-G) dx$ is drawn. Two curves are shown. the lower curve corresponds to the precise numerical solution, i.e. to $\int_0^{\infty} \exp(-G) dx$. The upper curve corresponds to $B(z=\infty)/A = \int_0^z \exp(-G_2) dx$. This curve is very close to numerical solution. It is very important that both curves resemble a straight line. So, already the linear approximation on A corresponding to the account of the first leading (linear) term will be good. It means that in the last expression one can take instead of $B(z=\infty)$ the value $A \int_0^{\infty} \exp(-G_0) dx$ (on the base of the first iteration one puts $\sim A \int_0^{\infty} f_1 dx$).

2.3 Wide spectrum of active centers

Three regions were extracted in the spectrum of activities: the region of active centers (they are almost exhausted), the region of centers with small activity (they remain practically free during the whole process) and the intermediate region. In the majority of the situations the

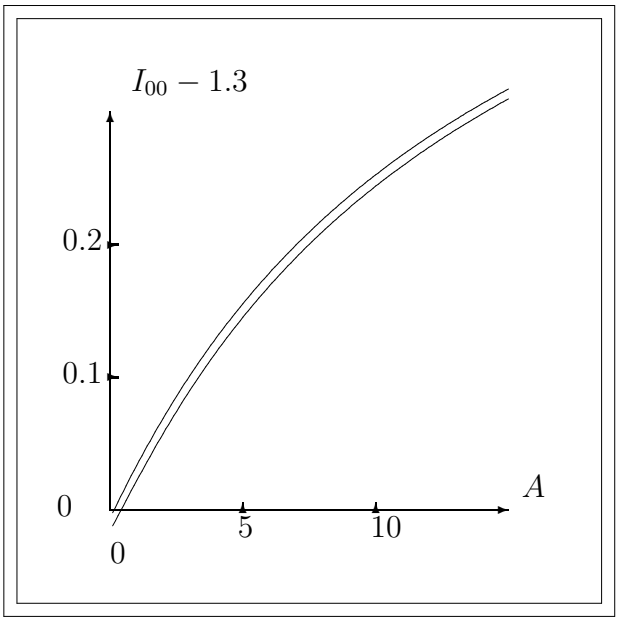

Figure 10.
The form of I_{00} as a function of A.

intermediate region has relatively small size in comparison with the active region (the passive region has no size - it can be spread to infinity). Then one can fulfill some further simplifications.

One can transmit the point $w = 0$ to the special activity for which

$$\theta \mid_{w=0} (\infty) = \frac{1}{2} \quad ,$$

i.e. the half of the centers became the centers of droplets. Then the system of the condensation equations after the rescaling of w can be written as

$$g = a_0 \exp(w) \int_0^z (z - x)^3 \exp(-G)\theta dx \quad , \tag{69}$$

$$G = \int_{-\infty}^{w_+} g(w) dw \quad , \tag{70}$$

$$\theta = \exp(-a_1 \exp(w) \int_0^z \exp(-G) dx) \quad , \tag{71}$$

where w_+ is the upper boundary of spectrum and $a_0,\ a_1$ are some constants. Having rescaled z, x one can put $a_0 = 1$. The condition of the choice for $w = 0$ gives:

$$a_1 = \frac{\ln 2}{\int_0^\infty \exp(-G) dx} \quad . \tag{72}$$

So, there remains only one parameter w_+.

Let us explicitly extract the intermediate and the active regions. One can see that for two different activities w_1 and w_2 the following equation is valid

$$\frac{\ln(\theta(w_1,x))}{\exp(w_1)} = \frac{\ln(\theta(w_2,x))}{\exp(w_2)} \quad . \tag{73}$$

The same is valid for the final values of θ. The value of $\ln(\theta(w,x))/\exp(w)$ is invariant for the different activities in one and the same process. So, one can put $w = w_{++} \equiv 2 \div 3$ as the boundary between the active region and the intermediate region. In the same manner one can separate the region of the passive centers by the boundary $w_{--} = -w_{++}$. One can neglect the substance in the droplets on the passive centers and get[4]

$$G \approx \int_{w_{--}}^{w_+} g(w)dw \quad . \tag{74}$$

One can denote by $n_\infty G_+$ the number of the substance molecules in the droplets formed on the active centers. The system of the condensation equations can be rewritten as

$$g = a_0 \exp(w) \int_0^z (z-x)^3 \exp(-G)dx \quad ,$$

$$G = \int_{-\infty}^{w_{++}} g(w)dw + G_+ \quad ,$$

$$\theta = \exp(-a_1 \exp(w) \int_0^z \exp(-G)dx) \quad .$$

Now one can write an evident expression for G_+

$$G_+ = \frac{\eta_*}{n_\infty}(w_+ - w_{++})z^3 \quad . \tag{75}$$

The system of the condensation equations now is the following one

$$g = a_0 \exp(w) \int_0^z (z-x)^3 \exp(-G)dx \quad ,$$

$$G = \int_{-\infty}^{w_{++}} g(w)dw + \frac{\eta_*}{n_\infty}(w_+ - w_{++})z^3 \quad ,$$

$$\theta = \exp(-a_1 \exp(w) \int_0^z \exp(-G)dx) \quad .$$

The value of w_{++} is universal, but the coefficient in the term $\eta_*(w_+ - w_{++})z^3/n_\infty$ depends on parameters.

Having defined

$$G_- = \int_{-\infty}^{w_{++}} g(w)dw \quad , \tag{76}$$

one can propose the following estimate

$$G_- \leq (w_{++} - w_{--})\frac{\eta_*}{n_\infty}z^3 \quad . \tag{77}$$

[4]The absence of the active and intermediate regions ($w_+ < w_{--}$) means that the condensation occurs in the pseudo homogeneous way.

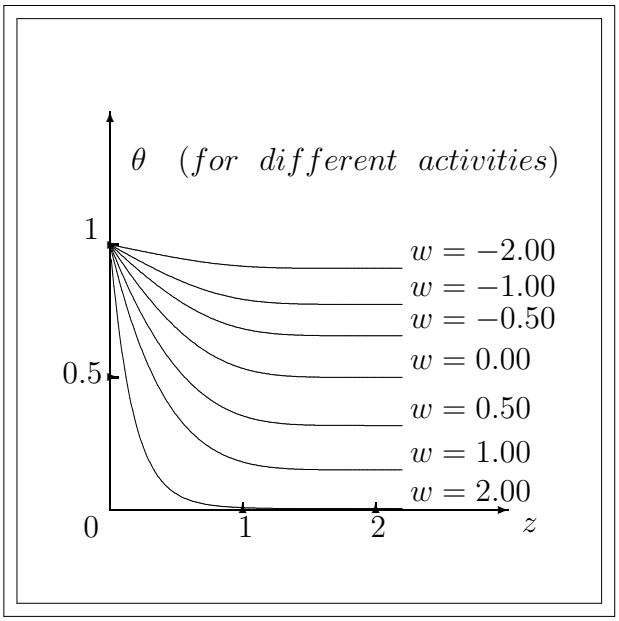

Figure 11.
Behavior of θ as a function of x for different w.

When

$$w_+ - w_{++} \gg w_{++} - w_{--} \sim 4 \div 6$$

one can approximately get

$$G = \frac{\eta_*}{n_\infty}(w_+ - w_{++})z^3 \quad .$$

Then the first equation isn't necessary at all. So, there is no necessity to put a_0 to 1 and one can use the arbitrary scale to cancel another constant. The system looks like

$$\theta = \exp(-a_1 \exp(w) \int_0^z \exp(-G)dx) \quad ,$$

$$G = \frac{\eta_*}{n_\infty}(w_+ - w_{++})z^3 \quad .$$

Having rescaled x, z, one can put $\eta_*(w_+ - w_{++}) = n_\infty$ and the system looks like the universal expression:

$$\theta = \exp(-\frac{\ln 2}{\int_0^\infty \exp(-z^3)dx} \exp(w) \int_0^z \exp(-z^3)dx) \quad .$$

The behavior of θ as a function of z for the different values of w is shown in Fig. 11.

One has to stress that in the general case of quasi continuous spectrum all results concerning the intermediate approximate solution can be used. One has only to substitute the sum over all sorts of centers by the integral over activities with appropriate normalizing coefficient: $\sum_i \to \sim \int dw$.

Moreover, the procedure of intermediate approximate solution can be directly applied to the situation with a mixed quasi continuous spectrum of activities and some discrete δ-like peaks for several sorts of heterogeneous centers.

This remark completes the description of the nucleation for the decay on heterogeneous centers with different activities. Unfortunately there are no experimental investigations which can be compared with the theory. It is rather natural because earlier there were no formulas which could give any physical information and experimental investigations would give only some chaotic experimental data. Now one can easily check this theory. This publication can be regarded as an invitation to open experimental investigations in this field. One can use the same devices as for the ordinary homogeneous nucleation investigations and calculate the number of droplets. Experiments on this theory can give information about the properties of heterogeneous centers in complex systems. The special interest is to solve some extreme problems to produce mainly the droplets on a given sort of centers when there are several sorts of centers in the system. With the help of this theory this prolem can be solved.

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